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# Magneto-resistance and superparamagnetism in magnetite films on MgO and MgAl<sub>2</sub>O<sub>4</sub>

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## Abstract

The present study is a comparison of the resistive and magnetic properties of ultrathin epitaxial Fe<sub>3</sub>O<sub>4</sub> films grown on MgO(001) and MgAl<sub>2</sub>O<sub>4</sub>(001). Such films on MgO are known to contain anti-phase boundaries, which cause magneto-resistance in these films, an increased resistivity with respect to the bulk and superparamagnetic behaviour for films below 5 nm thickness. Ultrathin films on MgAl<sub>2</sub>O<sub>4</sub> show a very similar behaviour as the resistivity is also increased with respect to the bulk, but is still lower than the resistivity of films grown on MgO. This indicates a larger domain size in the films grown on MgAl<sub>2</sub>O<sub>4</sub>. This is supported by the observed magneto-resistance that is larger than for films grown on MgO. Mössbauer spectroscopy analysis of a 1.7 nm thick film on MgO indicates that all magnetic moments in the film are fluctuating, whereas for the film on MgAl<sub>2</sub>O<sub>4</sub> a sextet with a parabolic background is observed. This shows that some domains are small enough for the moment to fluctuate while in larger ones, the moments are fixed; this also indicates that the domains in the film on MgAl<sub>2</sub>O<sub>4</sub> are larger than in the film grown on MgO.

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**Keywords:** Magneto-resistance; Spin polarization; Superparamagnetism; Magnetite; Spinel

## 1. Introduction and experimental

Magnetite, Fe<sub>3</sub>O<sub>4</sub>, is an extensively studied material because of several interesting properties. It is a ferri-magnet with a high Curie temperature of 858 K and electronically conducting with highly spin-polarized conduction electrons. Consequently, it is an interesting candidate for magnetic recording media or spin-valve applications.

Epitaxial thin films of Fe<sub>3</sub>O<sub>4</sub> on MgO show magneto-resistance (MR) in contrast to bulk single crystals [1]. Several studies have shown that the Fe<sub>3</sub>O<sub>4</sub> films contain anti-phase boundaries (APBs) [2,3], that result from the fact that Fe<sub>3</sub>O<sub>4</sub> has a different symmetry than MgO and the lattice constant of Fe<sub>3</sub>O<sub>4</sub> ( $a = 8.397 \text{ \AA}$ ) is twice as large as the lattice constant of MgO ( $a = 4.212 \text{ \AA}$ ). When depositing Fe<sub>3</sub>O<sub>4</sub> on MgO, neighbouring growth

islands may be rotated or shifted with respect to each other, resulting in anti-phase boundaries. The magnetic coupling over a large fraction of these boundaries is anti-ferromagnetic. The anti-ferromagnetic APBs thus act as a barrier for the spin-polarized conduction electrons. Upon application of a magnetic field, the orientation of the spins at the boundary can be changed and the resistance decreases. This is why epitaxial films show MR and single crystals do not. The presence of the anti-phase boundaries is also the reason why the resistivity of the films is enhanced with respect to the bulk resistivity. The Verwey transition of these films is broadened and occurs at a lower temperature than for the bulk ( $T_v$  bulk  $\sim 120 \text{ K}$ ) and for very thin films, it is not present at all [4]. Ultrathin films below 5 nm also show superparamagnetic behaviour [5]. In these ultrathin films, the volume of the domains becomes small enough for the magnetization of the domains to fluctuate on the timescale of the measurement ( $10^{-8} \text{ s}$ ).

In order to obtain Fe<sub>3</sub>O<sub>4</sub> films with less anti-phase boundaries, we have also grown epitaxial Fe<sub>3</sub>O<sub>4</sub> films on

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MgAl<sub>2</sub>O<sub>4</sub>. Both the substrate and the epitaxial film exhibit the spinel type structure and symmetry and the lattice constant of MgAl<sub>2</sub>O<sub>4</sub> is 8.08 Å. Because of the similar crystal structure and lattice constants, the formation of APBs is not expected, but APBs in these films have been observed [6].

We have studied the resistivities and the MR behaviour of Fe<sub>3</sub>O<sub>4</sub> films grown on MgO and on MgAl<sub>2</sub>O<sub>4</sub>. The Fe<sub>3</sub>O<sub>4</sub> films have been grown on polished MgO(001) and MgAl<sub>2</sub>O<sub>4</sub>(001) substrates by molecular beam epitaxy (MBE) in an ultra high vacuum system with a base pressure of 10<sup>−10</sup> mbar. During growth, an iron flux of 1.2 Å/min and an oxygen pressure of 10<sup>−6</sup> mbar were applied at a substrate temperature of 523 K. The resistivity and MR measurements were performed in a commercial PPMS system (Quantum design). The current was measured in the four-point geometry along the [100] direction of the film. The magnetic field, up to 5 T, was applied both parallel and perpendicular to the film plane. To determine whether ultrathin Fe<sub>3</sub>O<sub>4</sub> films on MgAl<sub>2</sub>O<sub>4</sub> also show superparamagnetic behaviour, 1.7, 3.2 and 5 nm thick films have been grown with <sup>57</sup>Fe and studied at 300 K with conversion electron Mössbauer spectroscopy (CEMS).

## 2. Results/discussion

Fig. 1 shows the room temperature MR behaviour for 12 nm thick films on MgO and MgAl<sub>2</sub>O<sub>4</sub>, with the magnetic field applied perpendicular (Fig. 1a) and parallel to the film plane (Fig. 1b). The MR behaviour of Fe<sub>3</sub>O<sub>4</sub> films grown on MgO has been explained [7,8]. For perpendicular applied fields below the anisotropy field,  $H_{an}$ , a quadratic field dependence is obtained and above the uniaxial out of plane anisotropy field, it is

linear:

$$MR = -\frac{C_1}{H_{an}} H^2, \quad (1a)$$

$$MR = -C_1 H + D. \quad (1b)$$

A quadratic field dependence has also been obtained for the film on MgAl<sub>2</sub>O<sub>4</sub>, but for low fields the MR effect is slightly lower. This would mean a higher out of plane anisotropy field according to Eq. (1a). The out of plane resonance field as obtained from ferromagnetic resonance is indeed higher for Fe<sub>3</sub>O<sub>4</sub> films on MgAl<sub>2</sub>O<sub>4</sub> than for the films on MgO [9,10], indicating a higher anisotropy field.

For fields above the anisotropy field, a linear field dependence is expected (Eq. (1b)). The film on MgAl<sub>2</sub>O<sub>4</sub> has a much more linear field dependence than the film on MgO with a larger slope. In this field region, the MR effect is larger for the films grown on MgAl<sub>2</sub>O<sub>4</sub> than on MgO. This also happens for a parallel applied field, in which case the MR is expected to have a linear field dependence [7,8]. The MR curve for the film on MgAl<sub>2</sub>O<sub>4</sub> is more linear and the slope is larger than for the film on MgO.

The resistivity versus 1/T of 6, 12, 30 and 50 nm thick Fe<sub>3</sub>O<sub>4</sub> films on MgAl<sub>2</sub>O<sub>4</sub> is shown in Fig. 2a. There are similar trends as for the films grown on MgO [4]. The resistivity depends on the film thickness and increases with decreasing film thickness. Only the thickest film (50 nm) shows a clear Verwey transition around 107 K, which is lowered with respect to the bulk value of 120 K.

The resistivity of the 6 nm thick film on MgAl<sub>2</sub>O<sub>4</sub> has been compared to the resistivity of the 6 nm thick film grown on MgO in Fig. 2b. The resistivity of the film grown on MgAl<sub>2</sub>O<sub>4</sub> is about 1 order of magnitude lower than that for the film grown on MgO. The fact that both

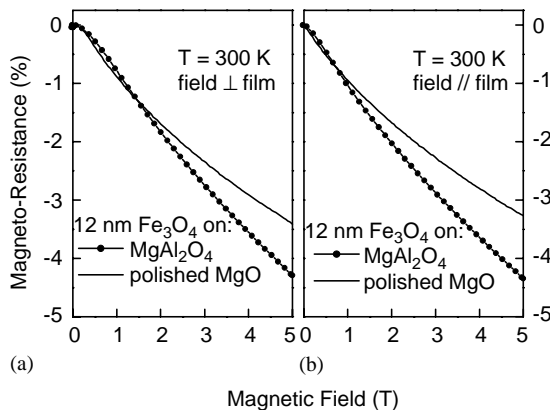


Fig. 1. MR at 300 K of 12 nm thick Fe<sub>3</sub>O<sub>4</sub> films on MgO (—) and MgAl<sub>2</sub>O<sub>4</sub> for magnetic fields up to 5 T applied (a) perpendicular to the film and (b) parallel to the film.

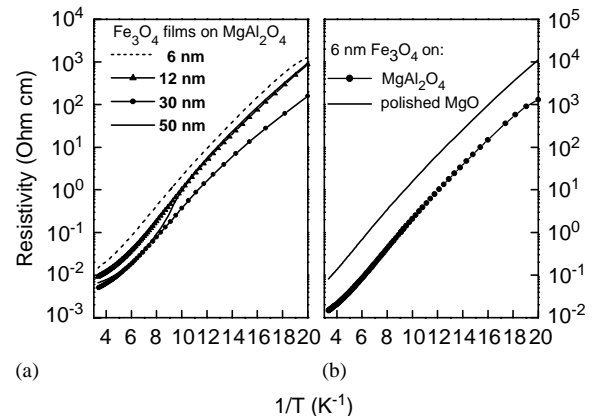


Fig. 2. (a) Resistivity versus 1/T of 6, 12, 30 and 50 nm thick Fe<sub>3</sub>O<sub>4</sub> films on MgAl<sub>2</sub>O<sub>4</sub>. Only the 50 nm thick films show a clear Verwey transition around 107 K. (b) Resistivity of 6 nm thick Fe<sub>3</sub>O<sub>4</sub> films on MgO (—) and MgAl<sub>2</sub>O<sub>4</sub>.

films show MR and have similar behaviour for the resistivity, implies that the films grown on  $\text{MgAl}_2\text{O}_4$  also contain anti-phase boundaries.

Mössbauer spectra of 5, 3.2 and 1.7 nm thick films on  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$  are shown in Fig. 3a–c, respectively. For films grown on  $\text{MgO}$ , it was already known that the spectra of the 1.7 nm thick film show motional narrowing, indicating a complete superparamagnetic behaviour [5]. As the film thickness increases to 3.2 nm, the sextet structure that is normally observed for bulk  $\text{Fe}_3\text{O}_4$  begins to appear, with a parabolic background due to some of the smallest domains still being superparamagnetic. For the 5 nm thick film, the background has almost vanished and the spectrum is like bulk  $\text{Fe}_3\text{O}_4$ . The 1.7 nm thick film on  $\text{MgAl}_2\text{O}_4$  still has a sextet component, but the parabolic background indicates a large degree of super-paramagnetism. The spectrum is very similar to that of the 3.2 nm thick film on  $\text{MgO}$  (Fig. 3b and c); it is therefore estimated that the domain size for the film on  $\text{MgAl}_2\text{O}_4$  is about twice as large as

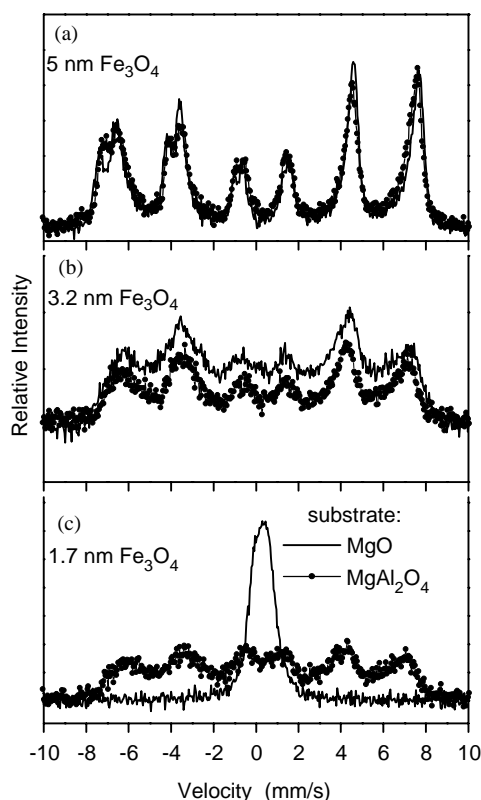


Fig. 3. CEMS spectra of  $^{57}\text{Fe}_3\text{O}_4$  films on  $\text{MgO}$  (—) and  $\text{MgAl}_2\text{O}_4$  for: (a) 5 nm thick film, (b) 3.2 nm thick film and (c) 1.7 nm thick film, showing that for the 1.7 nm thick film on  $\text{MgO}$ , all the magnetic moments fluctuate at the time scale of the measurement (superparamagnetism), but on  $\text{MgAl}_2\text{O}_4$  larger domains have a fixed moment and the parabolic background is due to the smallest domains still having fluctuating magnetic moments.

for the film on  $\text{MgO}$ . Relaxation of the Mössbauer spectra due to fluctuating spins at the interface was ruled out by depth-selective probe layers [5], where probe layers at the  $\text{MgO}/\text{Fe}_3\text{O}_4$  interface yielded exactly the same spectra as probe layers in the centre of the  $\text{Fe}_3\text{O}_4$  layer.

From a structural point of view, it was not expected that  $\text{Fe}_3\text{O}_4$  films on  $\text{MgAl}_2\text{O}_4$  consist of domains separated by anti-phase boundaries, because both compounds have the spinel-type structure. However, if the only restriction for the growth of the epitaxial film is the continuation of the oxygen sublattice, the formation of APBs is indeed possible on  $\text{MgAl}_2\text{O}_4$  substrates. The  $\text{Fe}_3\text{O}_4$  can then nucleate at 7 non-equivalent sites on the  $\text{MgAl}_2\text{O}_4$  substrate. Kleint et al. [6] have indeed observed anti-phase boundaries in  $\text{Fe}_3\text{O}_4$  films grown on  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$ , but do not mention whether there is a difference in domain size for the two different substrates. Another factor that has to be taken into account is the misfit. Due to the misfit of almost 4% between  $\text{Fe}_3\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ , the epitaxial films above the critical thickness will be relaxed generating interfacial misfit dislocations, which can lead to stacking faults.

To conclude, ultrathin magnetite films have been deposited on  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$  substrates. Films on both substrates show MR. The resistivity of the films on  $\text{MgAl}_2\text{O}_4$  increases with decreasing film thickness and only the thickest film (50 nm) shows a clear Verwey transition lowered with respect to the bulk value. This is similar to the resistivity behaviour of films grown on  $\text{MgO}$ . The resistivity of the films on  $\text{MgAl}_2\text{O}_4$  is, however, about 1 order of magnitude lower than that for the films on  $\text{MgO}$ , indicating a larger domain size. Mössbauer spectra of a 1.7 nm thick film on  $\text{MgO}$  show complete relaxation indicating that the magnetization of all domains is fluctuating, whereas the spectra for the film on  $\text{MgAl}_2\text{O}_4$  show a sextet with a parabolic background. Therefore, the magnetic moment of small domains is able to fluctuate, while the larger domains have a fixed moment, also indicating a larger domain size for the films on  $\text{MgAl}_2\text{O}_4$ .

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## References

- [1] J.M.D. Coey, A.E. Berkowitz, L.I. Balcells, F.F. Putris, F.T. Parker, Appl. Phys. Lett. 72 (1998) 743.

- [2] D.T. Margulies, F.T. Parker, M.L. Rudee, F.E. Spada, J.N. Chapman, P.R. Aitchison, A.E. Berkowitz, *Phys. Rev. Lett.* 79 (1997) 5162.
- [3] T. Hibma, F.C. Voogt, L. Niesen, P.A.A. van der Heijden, W.J.M. de Jonge, J.J.T.M. Donkers, P.J. van der Zaag, *J. Appl. Phys.* 85 (1999) 5291.
- [4] R.J.M. Van de Veerdonk, et al., *Mater. Res. Soc. Symp. Proc.* 401 (1996) 455.
- [5] F.C. Voogt, T.T.M. Palstra, L. Niesen, O.C. Rogojanu, M.A. James, T. Hibma, *Phys. Rev. B* 57 (1998) R8017.
- [6] C.A. Kleint, et al., *J. Phys. IV* 7 C1 (1997) 593.
- [7] W. Eerenstein, T.T.M. Palstra, S.S. Saxena, T. Hibma, *Phys. Rev. Lett.* 88 (2002) 247204.
- [8] W. Eerenstein, T.T.M. Palstra, T. Hibma, *Thin Solid Films* 400 (2001) 90.
- [9] S. Kale, et al., *Phys. Rev. B* 64 (2001) 205413.
- [10] P.A.A. van der Heijden, M.G. van Opstal, C.H.W. Swüste, P.H.J. Bloemen, J.M. Gaines, W.J.M. de Jonge, *J. Magn. Mater.* 182 (1998) 71.